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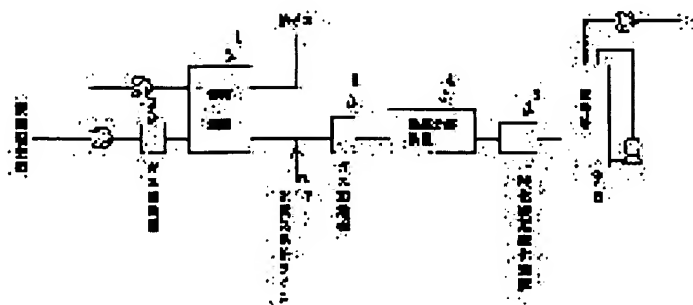
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(54) DEVICE FOR TREATING WASTE GAS CONTAINING ORGANIC HALOGEN COMPOUNDS

(57)Abstract:

PURPOSE: To effectively treat organic halogen compounds at low temperatures by installing a catalytic decomposition device packed with an organic halogen compound decomposition catalyst having a strong acidic point and a washing column for removing gaseous hydrogen halide generated by the decomposition of the organic halogen compounds.

CONSTITUTION: In a device where waste gas contg. organic halogen compounds (e.g. carbon tetrachloride) is treated and purified, a catalytic decomposition device 4 packed with an organic





halogen compound decomposition catalyst having a strong acidic point (e.g. zeolite) and a washing column 6 for removing gaseous halogen halide generated by the decomposition of the organic halogen compounds are installed. And in the preceding stage of the catalytic decomposition device 4 are provided with a concentrator 1 and gas heaters 2, 3. Further, in the poststage of the catalytic decomposition device 4 or the washing column 6, a carbon monoxide oxidizing device is provided, and in the prestage of the catalytic decomposition device 4, a steam feed line 7 is provided. And the organic halogen compound decomposition catalyst uses oxides of one or two or more of Si, Al, Ti, Zr, etc.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the processing unit of the exhaust gas containing an organic halogenated compound. After introducing into a catalyst cracking unit in detail the exhaust gas containing an organic halogenated compound and decomposing, it is related with the device from which the hydrogen halide which is a decomposition product of an organic halogenated compound in a washing tower is removed.

[0002]

[Description of the Prior Art]The organic halogenated compound is used in various fields, such as not only the raw material of a chemical but a detergent. In that case, the exhaust gas containing an organic halogenated compound is discharged. However, some of these organic halogenated compounds are considered as the causative agent of what has toxicity, such as carcinogenicity, or air pollution, and a causative agent of the ozone layer depletion which poses a problem by earth environment further, and greenhouse effect, and development of discharge control art is furthered.

[0003]As a processing unit of the exhaust gas containing an organic halogenated compound, the adsorption collecting method is known conventionally. However, in the adsorption collecting method, processing of the collected organic halogenated compound poses a problem. The impurity is usually being mixed in many cases, and before reusing, it is necessary for reuse to be directly possible when it is salvaged material with high purity, but to carry out distillation refining. It is necessary to process as waste fluid what is not recyclable in salvaged material, and it also has the problem that the cost for it starts.

[0004]In addition to the adsorption collecting method, a combustion method is also directly considered as a disposal method. However, the temperature of not less than 800 ** is directly required for a combustion method, and the temperature of not less than 1000 ** is needed depending on the kind of organic halogenated compound. In order to perform a combustion method at an elevated temperature directly, thermal NOx occurs, dioxin may generate further, and it becomes a cause of a new pollution problem.

[0005]

[Problem(s) to be Solved by the Invention]As mentioned above, the disposal method of the exhaust gas containing an organic halogenated compound also has a possibility of there being

a problem in post-processing and becoming a cause of a new pollution problem, and development of the processing unit of the exhaust gas containing a more effective organic halogenated compound is desired.

[0006]The result in which this invention persons examined the disposal method of the exhaust gas containing an organic halogenated compound, By introducing into a catalyst cracking unit directly in a high-concentration case, after condensing an organic halogenated compound with a concentration device, when an organic halogenated compound is low concentration, and removing hydrogen halide after that in a washing tower, It succeeded in processing the exhaust gas which contains an organic halogenated compound efficiently with the degree of low temperature, and the processing unit of this invention was completed.

[0007]

[Means for Solving the Problem]A processing unit of exhaust gas containing an organic halogenated compound, wherein this invention consists of a washing tower which removes hydrogen halide generated by disassembly of a catalyst cracking unit and an organic halogenated compound which were filled up with an organic halogen degradation catalyst which has a strong acid point is provided.

[0008]Next, this invention is explained in full detail.

[0009]An organic halogenated compound which is the target of processing by this invention, Are an included compound at least one sort in chlorine, fluoride, and bromine, and as an example, A carbon tetrachloride, chloroform, chloroethylene, 1,1,1-trichloroethane, 1,2-dichloroethane, tetrachloroethylene, trichloroethylene, chloroethylene, dichloromethane, trichlorofluoromethane, dichlorodifluoromethane, 1,1,2-trichloro-1,2,2-trifluoroethane, a methyl bromide, etc. are raised.

[0010]When an organic halogenated compound in exhaust gas is low concentration, an organic halogenated compound is condensed using a concentration device, and it introduces into a catalyst cracking unit. Concentration to be condensed is 1000 ppm or less preferably, and is 500 ppm or less still more preferably. It is especially possible to use a common honeycomb rotor type concentration device, a filled-up type adsorber, etc. as a concentration device, and it is not restricted. It is [adsorbent / which is used for a concentration device / zeolite / granular active carbon, fibrous activated carbon,] usable in all.

[0011]An organic halogenated compound condensed by a concentration device is introduced into a catalyst cracking unit.

[0012]A method of heating gas, before being introduced into a catalyst cracking unit, or a method of heating the catalyst tower itself can be used for a method to which a temperature required for catalyst decomposition is applied in a catalyst cracking unit. Direct heating according [a method of heating gas before being introduced into a catalyst device] to an electric heater, a combustion burner, a high-pressure-water steam, etc., and indirect heating are used. However, in the case of an inflammable high-concentration organic halogenated compound, since there is danger of explosion, indirect heating is preferred. A way a method of carrying out direct heating of the catalyst bed heats an outer wall of a catalyst tower with an electric heater and a combustion burner or a method of embedding an electric heater into a catalyst bed, a method embedding a pipe which let gas heated with a combustion burner etc. in a catalyst bed pass, etc. are used. As for construction material of a catalyst splitting column,

it is preferred to use acid-proof construction material, such as nickel, Inconel, nickel-Cr alloy, acid-proof metal of SUS310S grade or ceramic coating, and glass lining.

[0013]A mold in particular of a catalyst tower of a catalyst cracking unit is not limited, but it is [mold] usable in various gestalten, such as a filled-up type, a radian flow type, and a monolith type.

[0014]An organic halogen degradation catalyst used by this invention is what has a super-strong acid point, Are one sort or two sorts or more of oxides chosen from Si, aluminum, Ti, Zr, B, Nb, Cr, Ga, Mo, W, Y, Cu, Sr, La, Fe, Mn, and P, and as an example, Zeolite, silica alumina, a silica titania, titania zirconia, alumina boria, niobium oxide, etc. are raised. Sulfuric acid and phosphoric acid which are nonvolatile acid may be supported to these oxides, and a super-strong acid point may be made to increase to them.

[0015]Since poisoning may be carried out to halogen, such a catalyst needs ionic exchange or to make it support and to give endurance to halogen in an above catalyst independent in the precious metals, a transition metal, etc. It is also expectable that catalytic activity goes up the precious metals and a transition metal ionic exchange or by supporting.

[0016]As metal to embellish, Cu, Fe, Co, nickel, Mn, Pt, Pd, Rh, Au, Ag, Ir, W, Mo, V, Cd, Sn, and Pb are raised, and these one sort or two sorts or more are used. Ionic exchange or 0.05 - 20wt% of the amount of ornamentation metal to support is desirable.

[0017]These organic halogenated compound decomposition catalysts are solid acid catalysts which have a strong acid point. When temperature programmed desorption of pyridine is measured with a heating rate of 10 ** / min, passing helium gas at the rate of flow of 10 ml/min as carrier gas after a strong acid point in this invention made pyridine stick to a catalyst at 300 **, it is an acid site from which pyridine is desorbed at temperature of not less than 600 **. Either a Broensted acid point or the Lewes acid site is OK as a kind of acid site of a solid acid catalyst.

[0018]When an example of an organic halogen degradation catalyst is given, Co support H type mordenite, Fe support H type mordenite, They are W support titania zirconia multiple oxide, Pd support titania zirconia multiple oxide, Cr support titania zirconia multiple oxide, a Pt support alumina boria multiple oxide, Pt support niobium oxide, etc.

[0019]Although it is usable in various gestalten, such as honeycomb shape, a globular shape, a column, thin plate state, and mesh texture, a using form of a catalyst has preferred honeycomb shape with few pressure losses, when the amount of raw gas is large. Although decomposition temperature changes with organic halogenated compounds, it is 150-450 ** preferably 100-600 **.

[0020]It is necessary to add a steam depending on a kind of organic halogenated compound in the case of catalyst decomposition. For example, a compound which does not contain a hydrogen atom like par halocarbon is difficult for catalyst oxidative degradation, and needs an elevated temperature. However, it is easily decomposed by adding a steam. In the case of a carbon tetrachloride, by oxidative degradation, temperature of not less than 600 ** is needed, but in hydrolysis by addition of a steam, temperature of 200 ** can decompose 100%.

[0021]In disassembly of an organic halogenated compound, halogen gas which halogen gas was emitted in many cases and emitted in oxidative degradation by oxygen is more difficult to remove than hydrogen halide. However, by adding a steam, hydrogen halide can be made to

generate preferentially and water and an alkaline aqueous solution can remove easily. Thus, making a steam exist in reactant gas has many advantages. Oxygen to add and the water vapor content should just be the quantity more than the amount of theories which converts into carbon dioxide and hydrogen halide a carbon atom contained in an organic halogenated compound, and a halogen atom, and should just be the amount of theories of 1.5 times or more preferably. For example, the oxygen added should be not less than 1000 ppm, the steam should just be not less than 2000 ppm, and, in the case of gas containing 1000 ppm of carbon tetrachlorides, what is necessary is just not less than 1500 ppm of oxygen, and not less than 3000 ppm of steams preferably.

[0022]By a heat exchanger, as for gas decomposed with a catalyst cracking unit, it is preferred to carry out heat exchange to gas before decomposition, and it is useful for laborsaving of heating energy of gas. Since hydrogen halide is contained in gas, acid-proof things of construction material of a heat exchanger, such as acid-proof metal, a product made from ceramics, or a product made from glass lining, are preferred.

[0023]Gas decomposed with a catalyst cracking unit is introduced into a washing tower, and hydrogen halide which is a decomposition product of an organic halogenated compound is removed by water or alkaline aqueous solution.

[0024]General way of a washing tower pass water or an alkaline aqueous solution from the tower upper part, and establish a gas entrance in the lower part and it establishes a gas outlet in the upper part is preferred. An inside of a washing tower is filled up with a bulking agent, and a method of taking a large liquid contact area of gas is preferred. Since a bulking agent has a possibility of hydrogen halide dissolving and becoming aqueous acids, a product made from a plastic and a bulking agent made from ceramics are preferred. Although there are a method of discharging as it is after washing and a method of circulating through and using it with a pump, its latter is preferred, when using water as a penetrant remover and the former and an alkaline aqueous solution are used for a penetrant remover as a penetrant remover. Since acidity goes up and absorption efficiency worsens by absorbed hydrogen halide when circulating through and using a penetrant remover, it is preferred to perform operation which adds alkali moderately, maintains the pH of a penetrant remover, further always discharges some penetrant removers, and is replaced with a new penetrant remover. Although halogen ion of chlorine, fluoride, and bromine is contained in wastewater liquid, since concentration which can be discharged by effluent control is decided, it is necessary in these to remove fluoride. There are a method of contacting a substance which forms an insoluble salt in response to a penetrant remover to fluoride as a method of removing a fluorine ion, etc. For example, by contacting a penetrant remover to a calcium chloride, calcium fluoride insoluble to water is built and it can collect as settlings.

[0025]In this decomposition reaction, a ***** case has carbon monoxide according to a kind of organic halogenated compound, and a kind of organic halogenated compound decomposition catalyst. Since carbon monoxide is harmful, it is necessary to process it by a method of some kind. In this invention, a method of changing carbon monoxide into carbon dioxide using an oxidation catalyst is used. Restriction is not carried out that it is [oxidation catalyst] usable in things currently generally used, such as Pt-alumina, Pd-alumina, Pt-titania, Pd-titania, Pt-titania zirconia multiple oxide, and Pd-titania zirconia multiple oxide, and

specially. A carbon monoxide oxidation catalyst may be used, mixing with an organic halogenated compound decomposition catalyst, and may be installed immediately after a catalyst cracking unit and behind a washing tower as a carbon monoxide oxidation system. When using it, mixing with an organic halogenated compound decomposition catalyst, and when installing immediately after a catalyst cracking unit, in order to react to heated gas, there is newly no necessity for heating of gas, and it is not necessary to use excessive energy. However, as for a catalyst, since hydrogen halide exists in gas in these cases, it is preferred to use a catalyst of a titania type by which poisoning cannot be easily carried out to halogen. When installing behind a washing tower, since halogen hardly exists, there are no worries about poisoning of a catalyst, but since temperature of gas is falling to near the room temperature, it is necessary to heat to a temperature required for a reaction. As for reheated gas, it is preferred to collect heat through a heat exchanger.

[0026]

[Effect of the Invention] Processing of the organic halogenated compound which is related with the environmental clean-up which poses the present problem, and was conventionally emitted into the atmosphere as it was as exhaust gas is possible for this invention.

[0027]

[Example] Although an example is shown below, this invention is not limited to these.

[0028] The gas (other ingredients: dry air) containing example 11,1,1-trichloroethane 60ppm and 2% of a steam was prepared, and it was considered as processed gas.

[0029] Using the concentration device (1) as the honeycomb rotor type concentration device, the rotor portion used a honeycomb type activated carbon fiber 60 cm in diameter, and 40 cm in length.

[0030] an organic halogenated compound decomposition catalyst -- a titania zirconia multiple oxide (Ti/Zr=1.4) -- Cr -- 5wt% -- it supported and what was fabricated on diameter 1.5mmphi and a cylindrical pellet 5 mm in length was used. a carbon monoxide oxidation catalyst -- a titania zirconia multiple oxide (Ti/Zr=1.4) -- Pd -- 1wt% -- what supported what was supported to the honeycomb (2 mm of openings) of 30 cm in diameter and 40 cm in length cordierite was used.

[0031] Processed gas was introduced into the concentration device (1) by 1500-m³/Hr, and operated the number of rotations of the rotor as 6rph.

[0032] The air for desorption (a steam is included 2%) was introduced into the desorption part of the rotor by flow 3[of 150 m]/Hr after heating at 150 ** with the gas heaters for concentration devices (2).

[0033] The steam was supplied from the steam supply line (7) so that it might become 2wt% to this desorbed gas about a steam, and it introduced into the catalyst cracking unit (4) after heating at 400 ** with the gas heaters for catalyst cracking units (3). What filled the above-mentioned catalyst in a container 55 cm in diameter and 70 cm in length was used for the catalyst cracking unit (4). After the gas which came out from the catalyst cracking unit (4) was introduced into the carbon monoxide oxidation system (5) in which the above-mentioned carbon monoxide oxidation catalyst was filled and oxidized carbon monoxide, it was introduced into the washing tower (6) and washed by the NaOH aqueous solution 5%.

[0034] The presentation of the exhaust gas after washing is 1 ppm or less of hydrogen

chloride, and 1,1,1-trichloroethane, gaseous chlorine, and carbon monoxide were not contained.

[0035]as example 2 organic halogenated compound -- a titania zirconia multiple oxide (Ti/Zr=1.4) -- Pd -- 1wt%, [support and] It carried out by the same method as Example 1 except having used what was fabricated on diameter 1.5mmphi and a cylindrical pellet 5 mm in length, and not having used a carbon monoxide oxidation catalyst. The presentation of the exhaust gas after washing is 1 ppm or less of hydrogen chloride, and 1,1,1-trichloroethane, gaseous chlorine, and carbon monoxide were not contained.

[0036]using a carbon tetrachloride as example 3 organic halogenated compound -- as an organic halogenated compound decomposition catalyst -- H type mordenite (TOSOH CORP. make HSZ-620HOA) -- Co -- 2wt%, [support and] as a binder -- alumina -- 20wt% -- what was used and was fabricated on diameter 1.5mmphi and a cylindrical pellet 5 mm in length was used, gas cooking temperature was 220 **, and it carried out by the same method as Example 2 except not having used a carbon monoxide oxidation catalyst.

[0037]The presentation of the exhaust gas after washing is 1 ppm or less of hydrogen chloride, and a carbon tetrachloride, gaseous chlorine, and carbon monoxide were not contained.

[0038]1,1,2-TORIKUROROH 1,2,2-trifluoroethane is used as example 4 organic halogenated compound, as an organic halogenated compound decomposition catalyst -- a titania zirconia multiple oxide (Ti/Zr=1.4) -- W -- 2wt% -- it supported and carried out by the same method as Example 1 except having used what was fabricated on diameter 1.5mmphi and a cylindrical pellet 5 mm in length.

[0039]Hydrogen chloride and hydrogen fluoride of the presentation of the exhaust gas after washing are 1 ppm or less, and 1,1,2-TORIKUROROH 1,2,2-trifluoroethane, gaseous chlorine, fluorine gas, and carbon monoxide were not contained.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]Drawing 1 is one example of the flow plan of the device of this invention.

[Description of Notations]

- 1 -- Concentration device
- 2 -- Gas heaters for concentration devices
- 3 -- Gas heaters for catalyst cracking units
- 4 -- Catalyst cracking unit
- 5 -- Carbon monoxide cracking unit
- 6 -- Washing tower
- 7 -- Steam supply line

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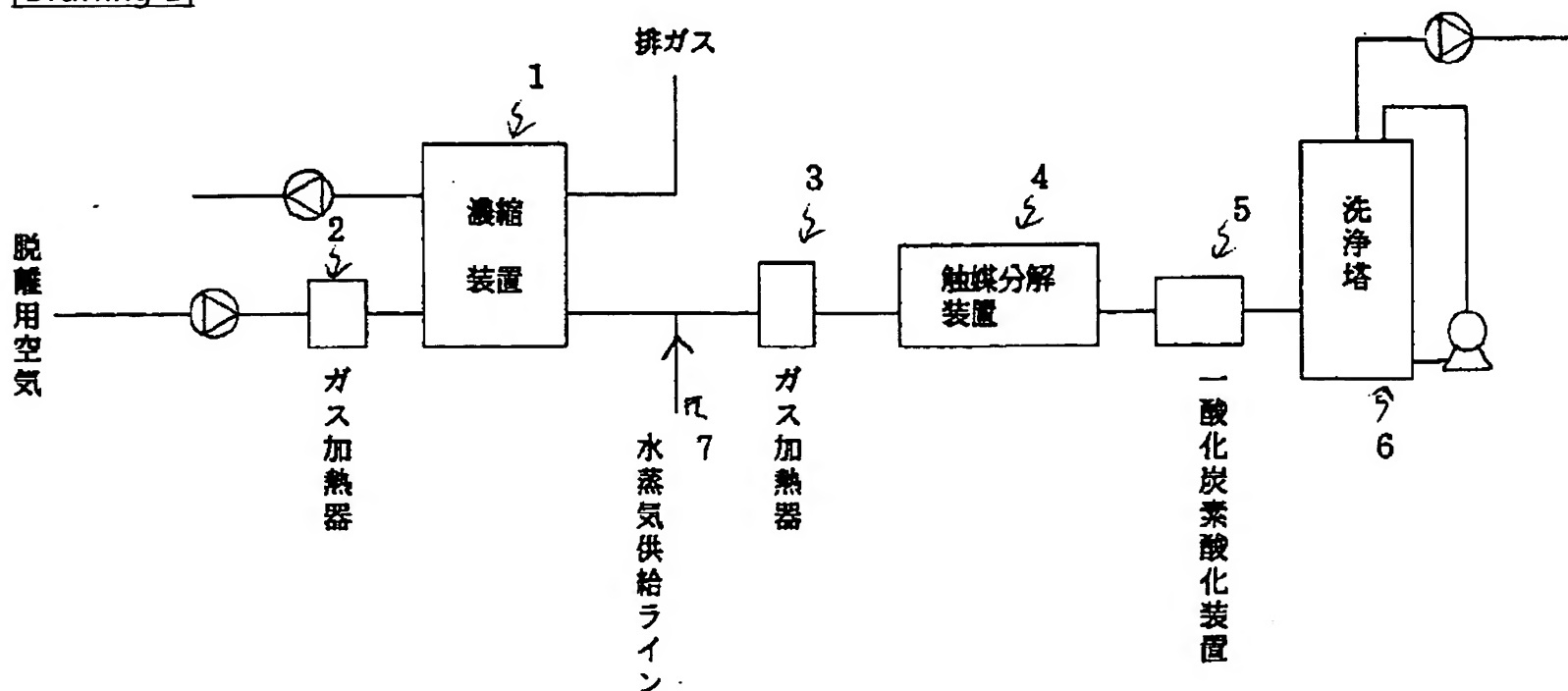
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DRAWINGS

[Drawing 1]



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